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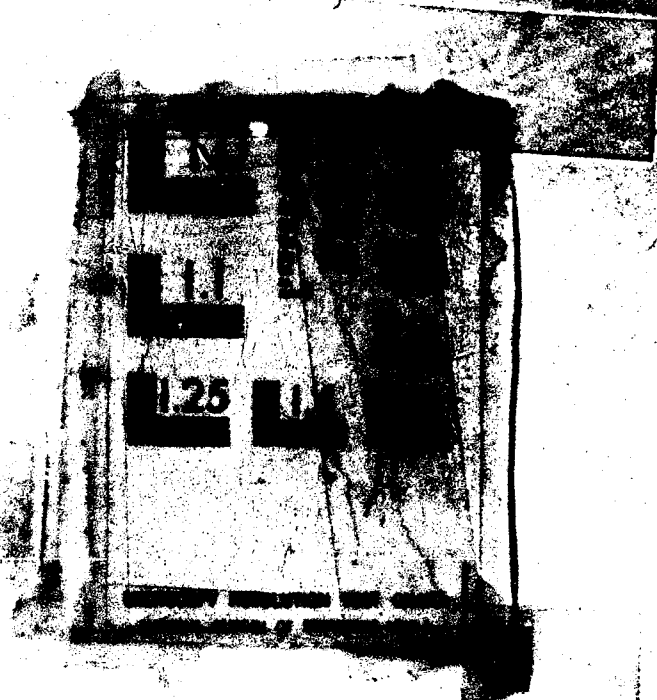
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The Interaction of Complexes $\text{Mn}(\text{PFhMe}_2)\text{Br}_2$ and $\text{Mn}(\text{PEt}_3)\text{Br}_2$ with Sulfur Dioxide

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Abstract

The interactions of the complexes $\text{Mn}(\text{PFhMe}_2)\text{Br}_2$ and $\text{Mn}(\text{PEt}_3)\text{Br}_2$ as films with SO_2 and S^{18}O_2 have been investigated using infrared spectroscopy as an analytical probe. It is clear from these preliminary studies that two types of complexes with SO_2 have been formed. When the MnLBr_2 films were exposed to low pressures of SO_2 for relatively short times, an $\text{MnLBr}_2/\text{SO}_2$ complex formed reversibly in that the SO_2 could be removed by prolonged evacuation. On the other hand, lengthy exposure of the MnLBr_2 films to higher pressures of SO_2 caused the irreversible formation of a complex having stoichiometry $\text{MnLBr}_2 \cdot 1/2\text{SO}_2$. It is probable that the SO_2 bonds in some type of bridging fashion in both of the types of $\text{MnLBr}_2/\text{SO}_2$ complexes.

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There has been considerable recent interest in complexes of the form MnX_2 (L-tertiary phosphine, X=anion) and their interaction with dioxygen.^{1,2} Infrared work in these laboratories concerning films of the complexes has shown that the complexes do exist and that some do interact reversibly with dioxygen, the extent of which is markedly dependent upon the nature of the tertiary phosphine ligand.^{3,4} All of the complexes studied here, however, exhibit competing irreversible decay channels at room temperature to the corresponding phosphine oxide complexes.^{3,4} The purpose of this note is to report infrared data concerning the interaction of the complex films with sulfur dioxide.

The complex films studied here were prepared by sublimation of $MnBr_2$ onto a KBr infrared window followed by heating to ca. 473 K in a specially designed infrared cell^{3,4} at 10^{-6} Torr to remove all water. Then the dry $MnBr_2$ films were exposed to either $PFMe_2$ or PEt_3 in a cell to form the $MnLX_2$ complex films. Extensive evacuation at 10^{-6} Torr was employed to remove all traces of excess phosphine. The films thus prepared were exposed to SO_2 /evacuation cycles with infrared spectra (Perkin-Elmer Models 580 or 983 with data station) being monitored at appropriate intervals. Since $SO_2(g)$ exhibits infrared bands near 520, 1150, and 1360 cm^{-1} which might have interfered with resolution of the complex bands, the cell was always briefly evacuated following SO_2 exposure immediately before infrared analysis.

Figure 1 shows the infrared spectra corresponding to the $Mn(PFMe_2)Br_2$ complex film interacting with SO_2 . A comparison of Fig. 1b and 1a reveals that new infrared bands at $SO_2(S^{18}O_2)$: 412(410), 445(440), 525(515), 785(780), 995(950), 1002(968), and 1075(1028) cm^{-1} appear which can be attributed to a new complex(es) formed from the reaction of SO_2 with

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Figure 1 shows a series of experiments for $\text{NaLiBr}_2/\text{SO}_2$ in which does not shift upon evacuation. This band can be assigned to a ligand vibrational mode (the ν_2) which is perturbed due to the presence of SO_2 ; this band was also observed to be perturbed by the presence of dimethyl ether. All of the bands mentioned above returned partially upon evacuation at 10^{-6} Torr for 12 hr (Fig. 1c). We have been able to observe cycling of the intensities of these bands upon evacuation/evacuation for up to three cycles; i.e., 12 hr evacuation is required to essentially remove the SO_2 . However, upon lengthy exposure (72 hr) at high pressure (120 Torr) spectrum 1d resulted which could not be recovered by lengthy evacuation. The bands at 995, 1002, and 1075 cm^{-1} for the spectrum 1d are obviously SO_2 in itself and obviously correspond to SO_2 stretching vibrational modes; the fact that three such bands were present indicates that more than one type of complex is probably being formed. The other bands, the bands at 612 and 645 cm^{-1} shifted little upon evacuation; therefore, these bands could correspond to SO_2 modes. The bands at 865, 910, and 970 cm^{-1} do shift appreciably when SO_2 is removed and correspond to SO_2 modes.

Figure 2 shows a similar series of experiments for $\text{NaLiBr}_2/\text{SO}_2$ interacting with SO_2 . Band positions for SO_2 complex spectra are shown in parentheses. Again reversibility was observed as long as exposure time and pressure were minimized. It is clear that at least two types of $\text{NaLiBr}_2/\text{SO}_2$ complexes were formed in these experiments - one in which the SO_2 bands reversibly and one in which the SO_2 is coordinated in an irreversible fashion. Comparison of the intensities of the 865, 910, and 970 cm^{-1} bands in spectra 2d and 2e reveals that the reversible complex can decompose to the irreversible one even during evacuation following high SO_2 exposures.

Both samples of the two final irreversible SO_2 complexes were prepared under identical conditions in a similar complexity analogous to the sample treatment conditions for the complex films. The IR analysis of the two final irreversible SO_2 complex revealed that the stoichiometry for each was $\text{MnCl}_2 \cdot 1/2\text{SO}_2$.⁵ This data along with the observation of intense infrared bands in the $800\text{--}1200\text{ cm}^{-1}$ regions of the spectra imply that the two forms of each complex contain SO_2 bonded in a bridging mode,⁶ with more than one atom of Mn involved in the bridge. Final structure determination must await X-ray crystallographic data.

It should be noted that Maitliffe and coworkers have reported recently the reaction of SO_2 with several metal complexes in toluene solution and in toluene slurries.⁷ They report a stoichiometry of $\text{MnCl}_2 \cdot 2/3\text{SO}_2$ for their solution studies, and they were not able to observe reversibility. Furthermore, they report prominent infrared bands in the $1100\text{--}1300\text{ cm}^{-1}$ region which are not observed for the $\text{MnCl}_2 \cdot 1/2\text{SO}_2$ complex film. However, their experimental conditions (liquid phase, 760 mm Hg SO_2 exposure for 48 hr) were markedly different than those used in this work; thus it is possible that a reversible complex was formed also in their work, but converted to an irreversible product before analysis.

Acknowledgments

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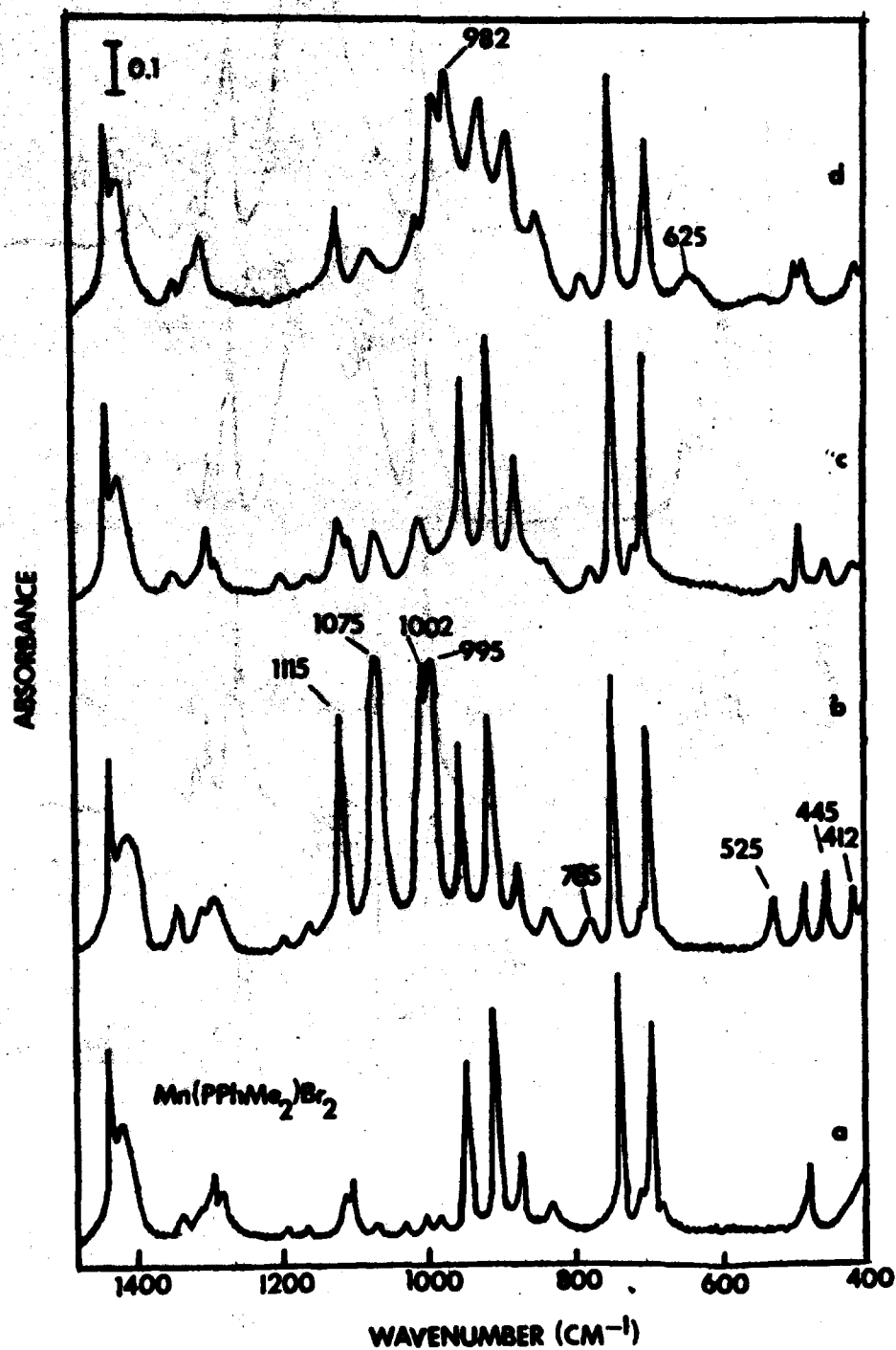
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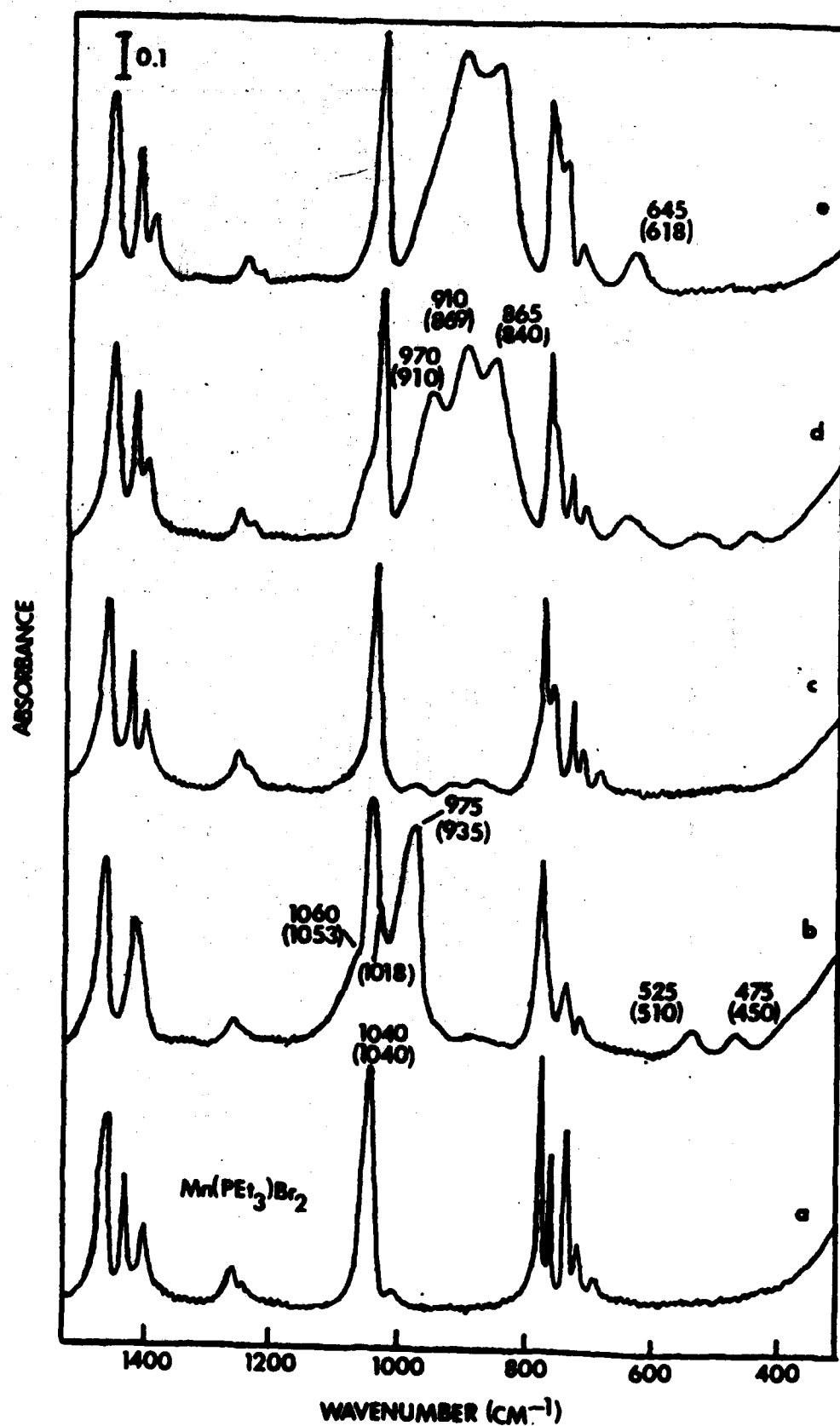
Figure Captions

Figure 1. The infrared spectra of a $\text{Mn}(\text{PFhMe}_2)\text{Br}_2$ film.:

(a) following initial preparation; (b) following exposure to 50 Torr SO_2 for 24 hr at 298 K and then brief evacuation; (c) following an evacuation cycle for 12 hr at 10^{-6} Torr at 298 K; (d) following exposure to 120 Torr SO_2 for 72 hr at 298 K and lengthy evacuation.

Figure 2. The infrared spectra of a $\text{Mn}(\text{PEt}_3)\text{Br}_2$ film: (a) following initial preparation; (b) following exposure to 15 Torr SO_2 for 15 min at 298 K and then brief evacuation; (c) following an evacuation cycle for 24 hr at 10^{-6} Torr at 298 K; (d) following exposure to 50 Torr SO_2 for 24 hr at 298 K and then brief evacuation; (e) following evacuation for 24 hr at 10^{-6} Torr at 298 K. Band positions for analogous S^{18}O_2 complex spectra are given in parentheses.





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